

Intrinsic Correlation between Hardness and Elasticity in Polycrystalline Materials and Bulk Metallic Glasses

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Abstract

Though extensively studied, hardness, defined as the resistance of a material to deformation, still remains a challenging issue for a formal theoretical description due to its inherent mechanical complexity. The widely applied Teter's empirical correlation between hardness and shear modulus has been considered to be not always valid for a large variety of materials. Here, inspired by the classical work on Pugh's modulus ratio, we develop a theoretical model which establishes a robust correlation between hardness and elasticity for a wide class of materials, including bulk metallic glasses, with results in very good agreement with experiment. The simplified form of our model also provides an unambiguous theoretical evidence for Teter's empirical correlation.

Keywords: Hardness, Elasticity, Bulk Metallic Glass, Polycrystalline Materials

1. Introduction

Despite the great efforts, to understand the theory of hardness and to design new ultrahard materials is still very challenging for materials scientists [1, 2, 3, 4]. During the past few years, several semi-empirical theoretical models [5, 6, 7, 8, 9] have been developed to estimate hardness of materials based on: (i) the bond length, charge density, and ionicity [5], (ii) the strength of the chemical bonds [6], (iii) the thermodynamical concept of energy density per chemical bonding [7], and (iv) the connection between the bond electron-holding energy and hardness through electronegativity [8], and (v) the temperature-dependent constraint theory for hardness of multicomponent bulk metallic glasses (BMGs) [9]. Experimentally, hardness is a highly complex property since the applied stress may be dependent on the crystallographic orientations, the loading forces and the size of the indenters. In addition, hardness is also characterized by the ability to resist to both elastic and irreversible plastic deformations and can be affected significantly by defects (*i.e.*, dislocations) and grain sizes [10]. Therefore, hardness is not a quantity that can be easily determined in a well-defined absolute scale [1]. It has been often argued [13] that hardness measurements unavoidably suffer of an error of about 10%. All these aspects add huge complexity to a formal theoretical definition of hardness [5, 6, 7, 8, 9].

Within this context, to find a simple way to estimate hardness of real materials is highly desirable. Unlike hardness, the elastic properties of materials can be measured and calculated in a highly accurate manner. Therefore, it has been historically natural to seek a correlation between hardness and elasticity. The early linear correlation between the hardness and

bulk modulus (B) for several covalent crystals (diamond, Si, Ge, GaSb, InSb) was successfully established by Gilman and Cohen since 1950s [10, 11]. Nevertheless, successive studies demonstrated that a uniform linear correlation between hardness and bulk modulus does not really hold for a wide variety of materials [12, 1, 13], as illustrated in Fig. 1(a). Subsequently, Teter [12] established a better linear correlation between hardness and shear modulus (G), as illustrated in Fig. 1(b). This correlation suggests that the shear modulus, the resistance to reversible deformation under shear strain, can correctly provide an assessment of hardness for some materials. However, this correlation is not always successful, as discussed in Refs. [5, 13, 14]. For instance, tungsten carbide (WC) has a very large bulk modulus (439 GPa) and shear modulus (282 GPa) but its hardness is only 30 GPa [15], clearly violating the Teter's linear correlation [see Fig. 1(b)] [5]. Although the link between hardness and elastic shear modulus can be arguable, it is certain to say that the Teter's correlation grasped the key.

In this manuscript, following the spirit of Teter's empirical correlation, we successfully established a theoretical model on the hardness of materials through the introduction of the classic Pugh modulus ratio of G/B proposed in 1954 [16]. We found that the intrinsic correlation between hardness and elasticity of materials correctly predicts Vicker's hardness for a wide variety of crystalline materials as well as BMGs. Our results suggest that, if a material is intrinsically brittle (such as BMGs that fail in the elastic regime), its Vicker's hardness linearly correlates with the shear modulus ($H_v = 0.151 G$). This correlation also provides a robust theoretical evidence for the famous empirical correlation observed by Teter in 1998. On the other hand, our results demonstrate that the hardness of crystalline materials can be correlated with the product of the squared Pugh's modulus ratio and the shear modulus ($H_v = 2(k^2 G)^{0.585} - 3$ where k is Pugh's modulus ratio). This formula provides the firm evi-

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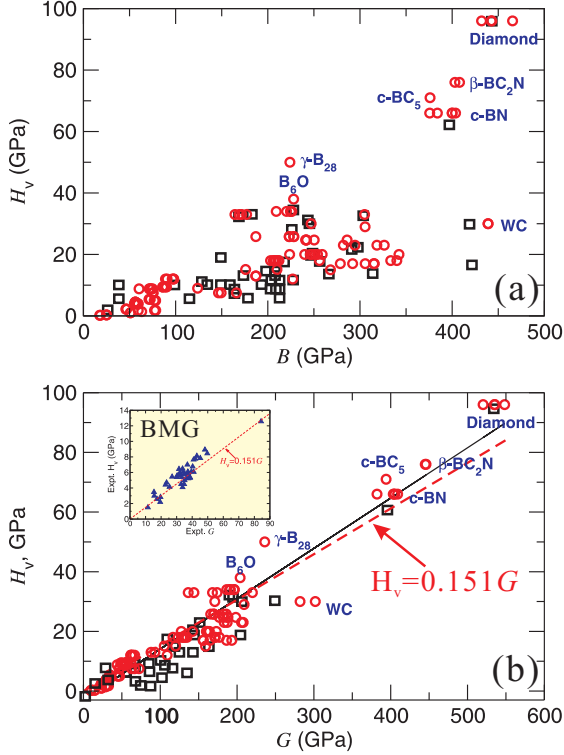


Figure 1: (Color online) Correlation of experimental Vickers hardness (H_v) with (a) bulk modulus (B) and with (b) shear modulus (G) for 39 compounds (Tables 2 and 3). Inset of panel (b): H_v vs. G for 37 BMGs (see Table 1). The solid line denotes empirical Teter's fitting values, whereas dashed lines correspond to the value derived from Eq. (6). The black and hollow squares denote data taken from Refs. ([12, 1]).

dence that the hardness not only correlates with shear modulus as observed by Teter, but also with bulk modulus as observed by Gilman *et al.* Our work combines those aspects that were previously argued strongly, and, most importantly, is capable to correctly predict the hardness of all compounds included in Teter's [12], Gilman's [4, 10], Gao's [5] and Simunek's [6] sets. Also, our model clearly demonstrates that the hardness of bulk metallic glasses is intrinsically based on the same fundamental theory as the crystalline materials. We believe that our relation represents a step forward for the understanding and predictability of hardness.

2. Model and Results

According to Vicker [10], the hardness of H_v is the ratio between the load force applied to the indenter, F , and the indentation surface area:

$$H_v = \frac{2F \sin(\theta/2)}{d^2}, \quad (1)$$

where d and θ are the mean indentation diagonal and angle between opposite faces of the diamond squared pyramid indenter, respectively (Fig. 2). In order to derive our model, we first assume that (i) the diamond squared pyramid indenter can be divided into four triangular based pyramid indenters and that

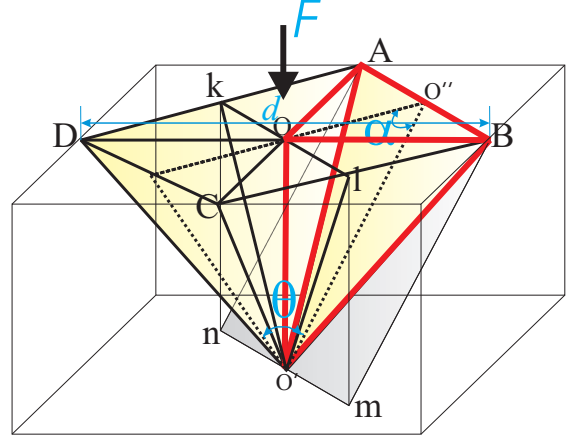


Figure 2: (Color online) Illustration of indentation in terms of the squared diamond pyramid indenter. The red framework highlights one of four triangular based pyramid indenters.

(ii) the Vicker's hardness is measured within the elastic scale. Then, for each triangular based pyramid, one can define the shear modulus G as,

$$G = \frac{F}{4A \tan(\alpha)} \quad (2)$$

which specifies the ratio between shear stress and the shear strain. In terms of our model the exact shear area A on which the shear force (F) acts is unknown. But, the deformation area A^* [$A^* = \frac{1}{8}d^2 \tan(\alpha)$] delimited by the kO' triangle is well defined by the indentation geometry. Therefore, we can express the exact shear area (A) as:

$$A = cA^* = \frac{c}{8}d^2 \tan(\alpha) \quad (3)$$

where c is the proportional coefficient. It is clear that under elastic shear deformation the deformation area (A^*) will be extremely small. However, upon real hardness measurements the deformation area (A^*) should be large enough so that the coefficient c can be safely neglected and $A \approx A^*$. Under this assumption, the equation (2) can be revised as following,

$$G = \frac{2F}{d^2 \tan^2(\alpha)} \quad (4)$$

Combining equations (1) and (4), the Vicker's hardness reads

$$H_v = G \tan^2(\alpha) \sin(\theta/2) = 0.92G \tan^2(\alpha) \quad (5)$$

where the term $\sin(\theta/2)$ is intrinsically determined by the indenter itself, which can be considered as a constant (originated from the Vicker's hardness, see equation (1)). For the diamond squared pyramid indenter with $\theta = 136^\circ$ then $\sin(\theta/2)$ is equal to 0.92 for Vicker's hardness measurement. In an ideal form of indentation, $\tan(\alpha) = 0.404$ because of $\alpha = \frac{(\pi-\theta)}{2.0}$ (c.f., Fig. 2). Therefore, the equation (5) can be simplified as,

$$H_v = 0.151G. \quad (6)$$

Equation (6) represents a robust theoretical evidence of the linear correlation behavior observed by Teter[12], as reflected by the data shown in Fig. 1(b). Residual discrepancies should be mainly attributed to the neglect of plastic deformation effects. Remarkably, we found that Eq. (6) is also valid for BMGs. Using the experimental shear modulus $G = 38.6$ (36.6) GPa [17] for $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ BMG, the estimated Vicker's hardness is 5.83 (5.53) GPa, in consistency with the experimental value of 5.38 GPa [17]. Similarly, for $\text{Fe}_{41}\text{Co}_7\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Y}_2$ BMG by using the experimental G (84.3 GPa [18]) we obtained $H_v = 12.7$ GPa, in nice accord with the measured Vicker's hardness of 12.57 ± 0.22 GPa [18]. As illustrated in the inset of Fig. 1(b), the agreement with the experimental values is highly satisfactory for all 37 BMGs collected here (see Table 1). Considering that BMGs are brittle materials without plastic fractures the data in the inset of Fig. 1(b) strongly convey that our proposed formula (Eq. 6) is intrinsically connected to the shear modulus of materials if they fail in an elastic regime.

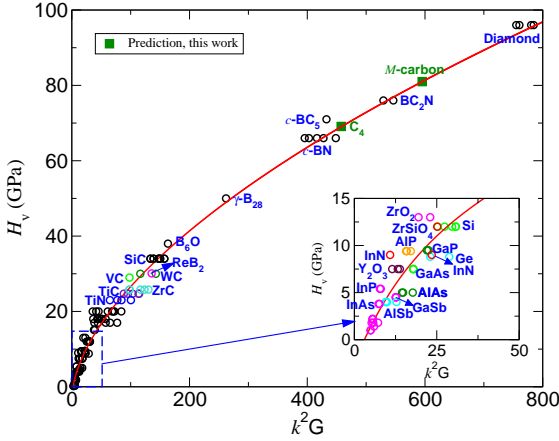


Figure 3: (Color online) Experimental Vicker's hardness as a function of the product k^2G ($k=G/B$). All data are collected from literature (see Tables 2 and 3).

It is highly difficult to realistically take plastic deformation into account in our modeling scheme. However, the indentation after a real hardness measurement shows the permanent plastic effect, which is, of course, reflected by the ratio $\frac{l_{00'}}{l_{00''}}$ [namely, equal to $\tan(\alpha)$] (see Fig. 2). Note that the depth of the indentation, $l_{00'}$, is parallel to the direction of shear deformation. We reasonably assume that its size should be closely correlated with the shear modulus of G , whereas the expansion wideness of the indentation, $l_{00''}$, is perpendicular to the direction of the loading force, hence, with almost little connection to the shear deformation. Therefore, the expansion wideness seems to reflect the ability to resist to compression effects, a property that should be related to bulk modulus, B . Accordingly, we proposed the following relation,

$$\tan(\alpha) \propto G/B \quad (7)$$

Finally, combining the equations (5) and (7), the hardness can be written as,

$$H_v \propto G(G/B)^2 \quad (8)$$

It is interesting to note that in Eq. (8) the ratio of G/B is the famous modulus ratio proposed by Pugh in as early as 1954 [16]. In his pioneer work, Pugh derived that the strain at fracture can be measured as $\epsilon \propto (B/G)^2$. Indeed, hardness can be defined as the resistance to the applied stress at the critical strain of ϵ that the system can sustain before yielding it to fracture. This clearly provides fundamental support for our model (Eq. 8). Importantly, Pugh also highlighted a relation between the elastic and plastic properties of pure polycrystalline metals and stated that G/B is closely correlated to the brittle and ductility of materials [16]: the higher the value of G/B is, the more brittle the materials would be [16]. Otherwise, the materials are expected to deform in a ductile manner with a low G/B value. This relation has been extensively accepted and applied not only to metal but also to high-strength materials [25, 26, 27]. In principles, the covalent materials (such as diamond and *c*-BN) have the highest hardness but they are obviously brittle with a larger Pugh modulus ratio. The strong covalent bonds indeed create a significant resistance to initialize the plastic flow to pin the dislocation, resulting in a quite high hardness. Conversely, ductile materials with a low Pugh's modulus ratio are characterized by metallic bonding and low hardness. It is thus highly reasonable to establish a correlation between hardness and the modulus ratio G/B in Eq. (8). Thus, we revise further the Eq. (8) in the following form,

$$H_v = Ck^m G^n; (k = G/B) \quad (9)$$

where H_v , G and B are the hardness (GPa), shear modulus (GPa) and bulk modulus (GPa), respectively. The parameter k is the Pugh's modulus ratio, namely, $k = G/B$. C is a proportional coefficient. In order to derive the parameters C , m and n , we first selected ten materials with diamond-like (diamond, *c*-BN, β -SiC, Si and Ge), zinc-blende (ZrC and AlN) and rock-salt structures (GaP, InSb and AlSb) because their hardness, bulk and shear moduli are well-known (see Tables 2 and 3). By analyzing these data we found that $C=1.887$, $m=1.171$ and $n = 0.591$. Hence, Eq. (9) becomes,

$$H_v = 1.887k^{1.171}G^{0.591} \approx 1.887(k^2G)^{0.585}. \quad (10)$$

In order to assess the validity of this relation, we plot in Fig. 3 H_v against k^2G for a series of compounds. These data show a clear and systematic trend with k^2G and firmly establish a direct relation between hardness and k^2G . By fitting the data of Fig. 3 and revising further Eq. (10) we arrive to the final formula:

$$H_v = 2(k^2G)^{0.585} - 3. \quad (11)$$

from which we see that the hardness correlates not only with the shear modulus but also with the bulk modulus. Physically, the bulk modulus only measures isotropic resistance to volume change under hydrostatic strain, whereas shear modulus responses to resistance to anisotropic shear strain. Although the

Table 1: The comparison between the predicted Vicker's hardness by Eq. (6) [$H_v = 0.151G$] and the experimental data for 37 bulk metallic glasses are shown, together with experimental Young modulus (E) and Shear modulus (G). The [XX];[YY] in the first column denotes the reference numbers: XX is the reference for elastic constants and YY is the reference for the Vicker's hardness.

Compounds	E	G	H_{calc}	H_{exp}
Fe ₄₁ Co ₇ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆ Y ₂ [18]	226	84.3	12.73	12.57
Ni ₅₀ Nb ₅₀ [19]	132	48.2	7.26	8.93
Ni ₄₀ Cu ₅ Ti ₁₇ Zr ₂₈ Al ₁₀ [20]	133.9	49.7	7.50	8.45
Ni _{39.8} Cu _{5.97} Ti _{15.92} Zr _{27.86} Al _{9.95} Si _{0.5} [20]	117	43	6.49	8.13
Ni ₄₀ Cu ₅ Ti _{16.5} Zr _{28.5} Al ₁₀ [20]	122	45.2	6.83	7.84
Ni ₄₅ Ti ₂₀ Zr ₂₅ Al ₁₀ [20]	114	42	6.34	7.76
Ni ₄₀ Cu ₆ Ti ₁₆ Zr ₂₈ Al ₁₀ [20]	111	40.9	6.18	7.65
{Zr ₄₁ Ti ₁₄ Cu _{12.5} Ni ₁₀ Be _{22.5} } ₉₈ Y ₂ [21]	107.6	40.3	6.09	6.76
Zr ₅₄ Al ₁₅ Ni ₁₀ Cu ₁₉ Y ₂ [21]	92.1	33.8	5.10	6.49
Zr ₅₃ Al ₁₄ Ni ₁₀ Cu ₁₉ Y ₄ [21]	86	31.5	4.76	6.44
Zr ₄₁ Ti ₁₄ Cu _{12.5} Ni ₈ Be _{22.5} C ₁ [21]	106	39.5	5.96	6.13
Zr _{46.75} Ti _{8.25} Cu _{7.5} Ni ₁₀ Be _{27.5} [19]	100	37.2	5.62	6.1
Zr ₄₈ Nb ₈ Cu ₁₄ Ni ₁₂ Be ₁₈ [21]	93.7	34.2	5.16	6.09
Zr ₃₄ Ti ₁₅ Cu ₁₀ Ni ₁₁ Be ₂₈ Y ₂ [21]	109.8	41	6.19	6.07
Zr ₅₇ Nb ₅ Cu _{15.4} Ni _{12.6} Al ₁₀ [19]	87.3	31.9	4.82	5.9
Zr ₄₈ Nb ₈ Cu ₁₂ Fe ₈ Be ₂₄ [21]	95.7	35.2	5.32	5.85
Zr ₄₀ Ti ₁₅ Cu ₁₁ Ni ₁₁ Be _{21.5} Y ₁ Mg _{0.5} [21]	94.2	34.7	5.24	5.74
Zr ₄₁ Ti ₁₄ Cu _{12.5} Ni ₁₀ Be _{22.5} [19];[21]	101	37.4	5.65	5.97
Zr ₄₁ Ti ₁₄ Cu _{12.5} Ni ₁₀ Be _{22.5} [19];[22]	101	37.4	5.65	5.4
Zr ₄₁ Ti ₁₄ Cu _{12.5} Ni ₁₀ Be _{22.5} [19];[23]	101	37.4	5.65	5.88
Zr ₄₁ Ti ₁₄ Cu _{12.5} Ni ₁₀ Be _{22.5} [19]	101	37.4	5.65	5.23
Zr ₆₅ Al ₁₀ Ni ₁₀ Cu ₁₅ [19]	83	30.3	4.58	5.6
Zr ₆₅ Al ₁₀ Ni ₁₀ Cu ₁₅ [19]	83	31	4.58	5.6
Zr ₅₇ Ti ₅ Cu ₂₀ Ni ₈ Al ₁₀ [19]	82	30.1	4.55	5.4
Cu ₆₀ Hf ₁₀ Zr ₂₀ Ti ₁₀ [19]	101	36.9	5.57	7
Cu ₅₀ Zr ₅₀ [19]	88.7	32.4	4.83	5.8
Cu ₅₀ Zr ₅₀ [19]	85	32	4.83	5.8
Cu ₅₀ Zr ₄₅ Al ₅ [19]	102	33.3	5.03	5.4
Pd ₄₀ Ni ₄₀ P ₂₀ [19];[17]	108	38.6	5.83	5.38
Pd ₄₀ Ni ₄₀ P ₂₀ [17]	–	36.6	5.53	5.38
Pd ₄₀ Ni ₄₀ P ₂₀ [19]	108	38.6	5.83	5.3
Pd ₄₀ Ni ₁₀ Cu ₃₀ P ₂₀ [19]	98	35.1	5.30	5
Pd _{77.5} Si _{16.5} Cu ₆ [19]	92.9	32.9	5.25	4.5
Pd _{77.5} Si _{16.5} Cu ₆ [19]	96	34.8	5.25	4.5
Pt ₆₀ Ni ₁₅ P ₂₅ [19]	96	33.8	5.10	4.1
Mg ₆₅ Cu ₂₅ Tb ₁₀ [19]	51.3	19.6	2.96	2.83
Nb ₆₀ Al ₁₀ Fe ₂₀ Co ₁₀ [19]	51.2	19.4	2.93	2.2
Ce ₇₀ Al ₁₀ Ni ₁₀ Cu ₁₀ [19]	30	11.5	1.74	1.5
Er ₅₅ Al ₂₅ Co ₂₀ [24]	70.72	27.08	4.09	5.45
Dy ₅₅ Al ₂₅ Co ₂₀ [24]	61.36	23.52	3.55	4.7
Tb ₅₅ Al ₂₅ Co ₂₀ [24]	59.53	22.85	3.45	4.42
Ho ₅₅ Al ₂₅ Co ₂₀ [24]	66.64	25.42	3.84	4.14
La ₅₅ Al ₂₅ Co ₂₀ [24]	40.9	15.42	2.33	3.48
La ₅₅ Al ₂₅ Cu ₁₀ Ni ₅ Co ₅ [24]	41.9	15.6	2.36	3
Pr ₅₅ Al ₂₅ Co ₂₀ [24]	45.9	17.35	2.62	2.58

bulk modulus was thought to be less directly connected with hardness [5], the Pugh's modulus ratio k clearly contributes to the Vicker's hardness. Equation (11) demonstrates that, if bulk modulus increases, hardness would decrease as long as the shear modulus remains unchanged, and vice versa. This behavior can be understood by the fact that if the Pugh's modulus ratio G/B gets smaller with increasing bulk modulus, the material would become more ductile. Its hardness can be thus expected to have a lower value. Taking the example, the compounds TiN and β -SiC have almost the same experimental shear moduli [28, 29] of 187.2 GPa and 191.4 GPa, respectively. However, the experimental bulk modulus of TiN (318.3 GPa)[28, 29] is larger by about 42% than that of β -SiC (224.7 GPa). In terms of our formula, β -SiC is found to be harder than TiN, in agreement with the experimental observations[5, 30] [Expt (Calc in this work): TiN with $H_v = 23$ (20) GPa and β -SiC with $H_v = 34$ (33) GPa].

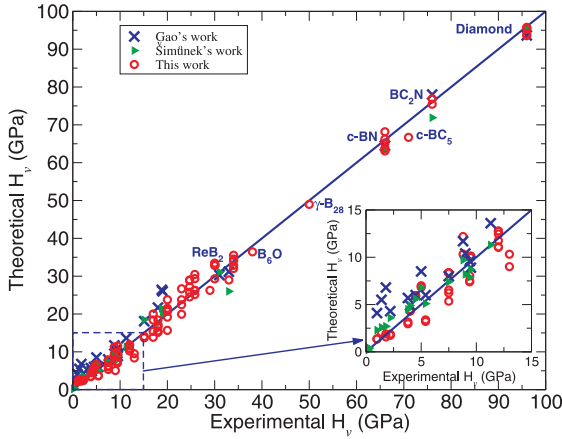


Figure 4: (Color online) Correlation between experimental and theoretical Vickers' hardness (H_v) for 39 compounds, as compared with the estimated data from the models [5, 6] (see Tables 2 and 3).

To further assess the performance of our model (Eq. 11) we show in Fig. 4 a comparison between the estimated and experimental values for a series of compounds (see Tables 2 and 3), confirming a good agreement. Also WC, which is wrongly found to be a superhard (49 GPa) material within Teter's linear correlation, is now predicted to have a Vicker's hardness of 29.3 GPa in very good accordance with experimental value (30 GPa [15]). In particular, Figs. 3 and 4 convey that our proposed formula reproduced very well the Vicker's hardness for all well-known superhard materials (Diamond [5, 6], BC_2N [12, 5, 6, 31], $c-BN$ [5, 6], $c-BC_5$ [32], and $\gamma-B_{28}$ [33, 34]).

The interesting case is the compound of ReB_2 , which was thought to be superhard [82]. Although its Vicker's hardness was debated extensively [82, 83, 84], there is now a wide-accepted consensus that its Vickers' hardness of 30.1 GPa at the large loading force of 4.9 N [45, 46]. Using the experimentally measured bulk and shear moduli [45] ($B = 273$ GPa and $G = 382$ GPa) and in terms of our Eq. (11), the Vicker's hardness is derived to be 32.9 GPa, in nice agreement with the experimental data [45].

Another attention has to be paid to the case of B_6O . Using the experimental bulk and shear moduli ($B = 230$ GPa and $G = 206$ GPa) [85], its Vicker's hardness is calculated to be 36.7 GPa within our current model. This value is well within the scale of the experimentally measured results from 32 to 38 GPa [42, 85] for polycrystalline boron suboxide sintered samples, although a Vicker's hardness of 45 GPa was reported for the single crystals under a loading force of 0.98 N [42]. Indeed, the light loading force of 0.98 N is not large enough to obtain a real hardness. It is thus expected to have a smaller hardness if a loading force larger than 0.98 N is applied. Our estimated value for B_6O is also in good agreement with the derived value of 37.3 GPa through a very recent thermodynamic model of hardness [86].

We further estimated two more phases of carbon (C_4 and M -carbon), which were suggested to be superhard [87, 88, 89, 90, 91]. Utilizing elastic shear and bulk moduli obtained in Ref. [89], the Vicker's hardness of C_4 is calculated to be 69.0 GPa (*c.f.*, Fig. 3) that is comparable to the superhard $c-BN$. Moreover, through using the calculated bulk and shear moduli ($B = 415$ GPa and $G = 468$ GPa [92]) for the M -carbon phase, we obtained its Vicker's hardness of 81.0 GPa (*c.f.*, Fig. 3), placing M -carbon in between BC_2N and diamond, agreeing well with the value (83.1 GPa) obtained by Šimunek's model [88].

In addition, from Fig. 4 all estimated data are in good agreement with those obtained from pervious models [5, 6]. Nevertheless, we would like to emphasize that, although our proposed model can reproduce well the results obtained by Cao's [5] and Šimunek's [6] models, the underlying mechanism is substantially different. Gao's and Šimunek's models are based on bond properties such as bond-length, charge density, ionicity and their strengths and coordinations in crystalline materials. Differently, our model depends totally on the so-called polycrystalline moduli (bulk and shear modulus as well as Pugh's modulus ratio), which indeed response directly to the abilities of resistance under loading forces for polycrystalline materials. As demonstrated above, for polycrystalline materials the introduced Pugh's modulus ratio in our model plays a crucial role in elucidating plastic deformation, which is intrinsically different from all known semi-empirical hardness models [5, 6, 7, 8, 9].

3. Discussion and Remarks

The hardness of a material is the intrinsic resistance to deformation when a force is applied [1]. Currently, a formal theoretical definition of hardness is still a challenge for materials scientists. The need for alternative superhard and ultrahard materials for modern technology has brought a surge of interest on modeling and predicting the hardness of real materials. In particular, in recent years several different semi-empirical models for hardness of polycrystalline covalent and ionic materials have been proposed. Gao's model is mainly based on bond length, charge density, and ionicity [5]. Šimunek's model employs the strength of the chemical bonds and its framework in crystalline materials [6]. Mukhanov's model utilizes the thermodynamical concept of energy density per chemical bond [7]. Li's model is mainly based on the bond electron-holding energy hardness through electronegativity [8]. Smedskjaer's model correctly predicts

Table 2: Comparison between theoretical values within our current model and experimental values as compared with available theoretical findings obtained through the models of Gao [5] and of Simunek [6]. Furthermore, the bulk and shear moduli are compiled in this table. In the last column, "e" and "c" denote elastic data (G and B) from direct experimental and theoretical calculations, respectively. The Pugh's modulus ratio k is compiled in this table. For details, see text. The [XX];[YY] in the first column denotes the reference numbers: XX is the reference for elastic constants and YY is the reference for the Vicker's hardness.

Compounds	G	B	k	H_{calc}	H_{exp}	H_{Gao}	$H_{Simunek}$	
Diamond [28];[5]	535.5	442.3	1.211	95.7	96	93.6	95.4	e
Diamond [28];[5]	548.3	465.5	1.178	93.9	96	93.6	95.4	c
Diamond [35];[5]	520.3	431.9	1.205	93.5	96	93.6	95.4	c
Diamond [12];[5]	535.0	443.0	1.208	95.4	96	93.6	95.4	e
BC ₂ N [36];[37]	446.0	403.0	1.107	76.9	76	78	71.9	c
BC ₂ N [12];[37]	445.0	408.0	1.091	75.4	76	78	71.9	e
BC ₅ [38];[32]	394.0	376.0	1.048	66.7	71			c
c-BN [18];[5]	405.4	400.0	1.014	65.2	66	64.5	63.2	e
c-BN [28];[5]	403.4	403.7	0.999	63.8	66	64.5	63.2	c
c-BN [28];[5]	382.2	375.7	1.017	63.1	66	64.5	63.2	c
c-BN [40];[5]	404.4	384.0	1.053	68.2	66	64.5	63.2	c
c-BN [12];[5]	409.0	400.0	1.023	66.2	66	64.5	63.2	e
γ -B ₂₈ [41];[33]	236.0	224.0	1.054	49.0	50			c
B ₆ O [12];[42]	204.0	228.0	0.895	36.4	38			e
β -SiC [28];[5]	191.4	224.7	0.852	32.8	34	30.3	31.1	e
β -SiC [28];[5]	196.6	224.9	0.874	34.5	34	30.3	31.1	c
β -SiC [43];[5]	190.2	209.2	0.909	35.5	34	30.3	31.1	c
β -SiC [44];[5]	186.5	220.3	0.846	32.0	34	30.3	31.1	e
β -SiC [12];[5]	196.0	226.0	0.867	34.1	34	30.3	31.1	e
SiO ₂ [12];[12]	220.0	305.0	0.721	29.0	33	30.4		e
ReB ₂ [45];[46]	273.0	382.0	0.715	32.9	30.1			e
WC [47];[5]	301.8	438.9	0.688	33.4	30	26.4	21.5	e
WC [9];[5]	282.0	439.0	0.642	29.3	30	26.4	21.5	e
B ₄ C [48];[12]	192.0	226.0	0.850	32.8	30 ^a			e
VC [This work];[6]	209.1	305.5	0.685	26.2	29		27.2	c
ZrC [49];[50]	169.7	223.1	0.761	26.3	25.8			e
ZrC [51];[50]	182.5	228.3	0.799	29.4	25.8			c
ZrC [51];[50]	185.9	228.0	0.815	30.5	25.8			c
ZrC [52];[50]	169.6	223.3	0.759	26.2	25.8			e
ZrC [12];[50]	166.0	223.0	0.744	25.2	25.8			e
TiC [49];[6]	182.2	242.0	0.753	27.1	24.7		18.8	e
TiC [53];[6]	176.9	250.3	0.707	24.5	24.7		18.8	c
TiC [54];[6]	198.3	286.0	0.693	25.8	24.7		18.8	c
TiC [55];[6]	187.8	241.7	0.777	28.8	24.7		18.8	e
TiC [12];[6]	188.0	241.0	0.780	29.0	24.7		18.8	e
TiN [56];[50]	183.2	282.0	0.650	22.5	23		18.7	c
TiN [57];[50]	187.2	318.3	0.588	20.0	23		18.7	e
TiN [58];[50]	205.8	294.6	0.699	26.7	23		18.7	c
TiN [59];[50]	207.9	326.3	0.637	23.8	23		18.7	c
RuO ₂ [60];[5]	142.2	251.3	0.566	15.7	20	20.6		c
RuO ₂ [61];[5]	173.0	248.0	0.698	23.7	20	20.6		c
Al ₂ O ₃ [40];[5]	161.0	240.0	0.671	21.5	20	20.6		c
Al ₂ O ₃ [40];[5]	160.0	259.0	0.618	19.2	20	20.6		c
Al ₂ O ₃ [62];[5]	164.0	254.0	0.646	20.7	20	20.6		e
Al ₂ O ₃ [12];[5]	162.0	246.0	0.659	21.1	20	20.6		e
NbC [63];[6]	171.0	333.0	0.513	15.5	18		18.3	c
NbC [52];[6]	171.7	340.0	0.505	15.2	18		18.3	e
AlN [40];[5]	134.7	206.0	0.654	18.4	18	21.7	17.6	c
AlN [64];[5]	130.2	212.1	0.614	16.5	18	21.7	17.6	c

^aB₄C was suggested to be very hard in Ref. [79]. Mukhanov *et al* recently predicted that the Vicker's hardness of B₄C was 45.0 GPa [86] in agreement with the reported experimental data of 45 GPa in Ref. [80] (see Table 1 in Ref. [86]). However, we also noted that Teter [12] ever summarized the hardness of B₄C with a value of 30±2 GPa. In addition, the experimental value of 32–35 GPa was recently summarized in the handbook [81]. Therefore, here we quoted the experimental Vicker's hardness of 30 GPa, as summarized by Teter in Ref. [12].

Table 3: (Table 2 continued)

Compounds	G	B	k	H_{calc}	H_{exp}	H_{Gao}	$H_{Simunek}$	
AlN [65];[5]	123.3	207.5	0.594	15.2	18	21.7	17.6	c
AlN [66];[5]	132.0	211.1	0.625	17	18	21.7	17.6	e
AlN [12];[5]	128.0	203.0	0.631	16.9	18	21.7	17.6	e
NbN [67];[6]	155.9	292.0	0.534	15.4	17		19.5	e
NbN [12];[6]	156.0	315.0	0.495	13.9	17		19.5	e
HfN [28];[50]	186.3	315.5	0.591	20.0	17			c
HfN [28];[50]	164.8	278.7	0.591	18.4	17			c
GaN [68];[5]	105.2	175.9	0.598	13.7	15.1	18.1	18.5	e
GaN [12];[5]	120.0	210.0	0.571	14.1	15.1	18.1	18.5	e
ZrO ₂ [40];[5]	88.0	187.0	0.471	8.4	13	10.8		c
ZrO ₂ [69];[5]	93.0	187.0	0.497	9.5	13	10.8		e
Si [49];[5]	66.6	97.9	0.680	11.8	12	13.6	11.3	e
Si [70];[5]	64.0	97.9	0.654	10.9	12	13.6	11.3	c
Si [70];[5]	63.2	90.7	0.697	11.8	12	13.6	11.3	c
Si [71];[5]	61.7	96.3	0.640	10.2	12	13.6	11.3	c
Si [71];[5]	61.7	89.0	0.693	11.5	12	13.6	11.3	c
GaP [52];[5]	55.7	88.2	0.631	9.3	9.5	8.9	8.7	e
GaP [49];[5]	55.8	88.8	0.628	9.2	9.5	8.9	8.7	e
GaP [47];[5]	56.1	88.6	0.633	9.4	9.5	8.9	8.7	e
GaP [73];[5]	61.9	89.7	0.690	11.5	9.5	8.9	8.7	c
AlP [74];[5]	49.0	86.0	0.570	7.1	9.4	9.6	7.9	e
AlP [73];[5]	51.8	90.0	0.575	7.5	9.4	9.6	7.9	c
AlP [75];[5]	48.8	86.0	0.567	7.0	9.4	9.6	7.9	c
InN [68];[6]	55.0	123.9	0.444	5.1	9	10.4	8.2	c
InN [74];[6]	77.0	139.6	0.552	9.7	9	10.4	8.2	c
Ge [70];[6]	53.1	72.2	0.736	11.3	8.8	11.7	9.7	c
Ge [70];[6]	43.8	60.3	0.726	9.5	8.8	11.7	9.7	c
GaAs [47];[5]	46.5	75.0	0.620	7.8	7.5	8.0	7.4	e
GaAs [72];[5]	46.7	75.5	0.619	7.8	7.5	8.0	7.4	e
GaAs [49];[5]	46.7	75.4	0.619	7.8	7.5	8.0	7.4	e
Y ₂ O ₃ [28];[5]	72.5	166.0	0.437	6.3	7.5	7.7		c
Y ₂ O ₃ [28];[5]	62.7	146.5	0.428	5.3	7.5	7.7		c
Y ₂ O ₃ [76];[5]	66.5	149.3	0.445	6.0	7.5	7.7		e
InP [72];[5]	34.3	71.1	0.483	3.8	5.4	6.0	5.1	e
InP [47];[5]	34.4	72.5	0.475	3.6	5.4	6.0	5.1	e
AlAs [77];[5]	44.8	77.9	0.575	6.7	5	8.5	6.8	e
AlAs [72];[5]	44.6	78.3	0.569	6.5	5	8.5	6.8	e
GaSb [72];[6]	34.2	56.3	0.607	5.8	4.5	6.0	5.6	e
GaSb [49];[6]	34.1	56.4	0.606	5.8	4.5	6.0	5.6	e
GaSb [47];[6]	34.3	56.3	0.608	5.8	4.5	6.0	5.6	e
AlSb [78];[5]	31.5	56.1	0.561	4.6	4	4.9	4.9	c
AlSb [72];[5]	31.9	58.2	0.549	4.5	4	4.9	4.9	e
AlSb [49];[5]	32.5	59.3	0.548	4.6	4	4.9	4.9	e
AlSb [47];[5]	31.9	58.2	0.549	4.5	4	4.9	4.9	e
InAs [72];[5]	29.5	57.9	0.509	3.6	3.8	5.7	4.5	e
InAs [49];[5]	29.5	59.1	0.499	3.4	3.8	5.7	4.5	e
InSb [47];[5]	23.0	46.9	0.490	2.4	2.2	4.3	3.6	e
InSb [72];[5]	22.9	46.5	0.492	2.4	2.2	4.3	3.6	e
InSb [49];[5]	22.9	46.0	0.498	2.5	2.2	4.3	3.6	e
ZnS [49];[6]	32.8	78.4	0.418	2.5	1.8		2.7	e
ZnS [47];[6]	31.5	77.1	0.408	2.3	1.8		2.7	e
ZnSe [47];[6]	28.8	63.1	0.456	2.7	1.4		2.6	e
ZnTe [47];[6]	23.4	51.0	0.459	2.1	1		2.3	e
ZnTe [49];[6]	23.4	51.0	0.459	2.1	1		2.3	e

the hardness of multicomponent BMGs through temperature-dependent constraint theory [9]. It has been noted that all the above models [5, 6, 7, 8, 9] have two major limitations: (i) Each one provides a satisfactory description only for a specific type of materials: Smedskjaer’s model treats BMGs with high degree of structural and topological disorder, whereas all other methods are essentially applicable to crystalline materials only, and (ii) they depends on different theoretical assumptions. Since these methods can only be used to predict the hardness of some specific materials a unified and general theory capable to account for the hardness of any material is still missing. If we look back the history of hardness, it can be easily found in literature that many scientists (Gilman, Cohen, Pugh and Teter) [10, 4, 11, 16, 12] have tried to create a correlation between the hardness and elasticity (a well defined quantity) since 1950s. The most successful empirical correlation was proposed by Teter in 1998 [12], who suggested that the hardness shows a quasi-linear correlation with the shear modulus. However, all these empirical correlations between hardness and bulk modulus (or shear modulus) turned out to be not fully successful. The main reason is that hardness indeed is a characteristic of a permanent plastic deformation, whereas the elasticity corresponds to the reversible elastic deformation. Therefore, there seems to be a general consensus on the fact that the hardness in general does not depends neither on the bulk modulus nor on the shear modulus for polycrystal materials. Indeed, these correlations were heavily debated in recent years.

In 1954 Pugh has proposed a relation between the elastic and plastic properties of pure polycrystalline metals and stated that the Pugh’s modulus ratio ($k = G/B$) represents a good criterion to identify the brittleness and ductility of materials [16]. It was found that material with a large k behaves in a more brittle manner, and that the higher the value of k is, the more brittle the materials are [16]. On the other side, materials with a low k are expected to deform in a more ductile way. Basically, as evidenced from Tables 2 and 3 we found that the Pugh’s modulus ratio, k , can be correlated with hardness. The hardest material, diamond, has the highest k value of about 1.2 and all widely accepted superhard materials have a highly large k value larger than 1.0. In addition, from Tables 2 and 3 one can see that with the progressive decrease of the Vicker’s hardness the k values get progressively smaller. Unlike the moduli of G and B , which only measures the elastic response, the Pugh’s modulus ratio seems to correlate much more reliably with hardness because it responses to both elasticity and plasticity, which are the most intrinsic features of hardness.

Therefore, through the introduction of the classic Pugh modulus ratio proposed in 1954 [16] and following the spirit of Teter’s empirical correlation, we have constructed a theoretical model of hardness. We proposed a new formula to calculate Vicker’s hardness, $H_v = 2(k^2G)^{0.585} - 3$, for polycrystalline materials. The most important aspect of our formula is that it correctly predict the hardness of all compounds dataset considered in several recent models [4, 5, 6, 7, 8, 12, 10] just under the condition of knowing the corresponding bulk and shear moduli. Furthermore, we proposed that, if a material is intrinsically brittle (such as BMGs), its Vicker’s hardness linearly correlates

with the shear modulus ($H_v = 0.151 G$). On the one hand, this simplified form provides a robust theoretical evidence why the famous empirical quasi-linear correlation observed by Teter in 1998 are right for some materials. On the other hand, we found for the first time the Vicker’s hardness can be linearly correlated with the shear modulus for BMGs (see Table 1). This is somehow unexpected because for BMGs there exists a universal correlation between the Yough’s modulus and the Vicker’s hardness as documented in Refs. [19, 93, 94].

Finally, we still want to point out that our model (Eq. 11) may be not accurate to predict the hardness of pure metals (or metallic-bonding dominated materials with a highly low Pugh’s modulus ratio). For instance, the hardness of fcc Al is estimated to be 1.3 GPa, which is significantly larger than the experimental Vicker’s hardness of 0.167 GPa. This is mainly due to the fact that ductile metals can locally accumulate plastic deformation prior to fracture, which has not been considered in our model.

In summary, via the aid of Pugh’s modulus ratio, our work provides the firm evidence that the hardness not only correlates with shear modulus as observed by Teter [12], but also with bulk modulus as observed by Gilman and Cohen [11, 10, 4]. By retaining the fundamental aspects of the previous proposed models, our model clearly demonstrates that the hardness of BMGs is intrinsically based on the same fundamental basis as the crystalline materials. Given the fact the elastic bulk and shear moduli can be accurately calculated by the state-of-the-art first-principles calculations, we believe that our finding is important for the community to design and develop ultra-hard/superhard materials and high-performance high-strength structural materials.

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